Part V: Generalized Kohn-Sham DFT

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Reduced density matrices

The wave-function ($\Psi$), defined in the Schrödinger equation, provides the complete description of a given system. There exists, however, an alternative formulation of quantum mechanics which uses **reduced density matrices**. Two types of density matrices are especially useful in quantum chemistry:

- **One-particle density matrix** $\gamma_1(x'_1, x_1)$:

  $$\gamma_1(x'_1, x_1) = N \int \cdots \int \psi(x'_1, x_2, \ldots, x_N)\psi^*(x_1, x_2, \ldots, x_N) dx_2 \cdots dx_N$$

- **Two-particle density matrix** $\gamma_2(x'_1, x'_2, x_1, x_2)$:

  $$\gamma_2(x'_1, x'_2, x_1, x_2) = \frac{N(N-1)}{2} \int \cdots \int \psi(x'_1, x'_2, \ldots, x_N)\psi^*(x_1, x_2, \ldots, x_N) dx_3 \cdots dx_N$$

where $x_i$ denotes the spin ($s_i$) and the space ($r_i$) coordinates.
Some useful relations involving reduced density matrices $\gamma_1$, $\gamma_2$

- $\gamma_1$ and $\gamma_2$ are Hermitian:

  $$\gamma_1(x'_1, x_1) = \gamma_1^*(x_1, x'_1)$$
  $$\gamma_2(x'_1, x'_2, x_1, x_2) = \gamma_2^*(x_1, x_2, x'_1, x'_2)$$

- $\gamma_1$ is normalized:

  $$\int \gamma_1(x_1, x_1) dx_1 = N$$

- Once $\gamma_2$ is known also $\gamma_1$ is known:

  $$\gamma_1(x'_1, x_1) = \frac{2}{N-1} \int \gamma_2(x'_1, x_2, x_1, x_2) dx_2$$

- $\gamma_1$ and $\gamma_2$ are positively defined:

  $$\gamma_1(x_1, x_1) \geq 0$$
  $$\gamma_2(x_1, x_2, x_1, x_2) \geq 0$$
Spin-less density matrices

One-particle spin-less density matrix:

\[
\rho_1(r'_1, r_1) = N \int \cdots \int \psi(r'_1, s_1, x_2, \ldots, x_N)\psi^*(r_1, s_1, x_2, \ldots, x_N) \, ds_1 \, dx_2 \cdots dx_N
\]

Two-particle spin-less density matrix:

\[
\rho_2(r'_1, r'_2, r_1, r_2) = \frac{N(N-1)}{2} \int \cdots \int \psi(r'_1, s_1, r'_2, s_2, \ldots, x_N)\psi^*(r_1, s_1, r_2, s_2, \ldots, x_N) \, ds_1 \, ds_2 \, dx_3 \cdots dx_N
\]

The diagonal element of the one-particle spin-less density matrix equals to the electron density:

\[
\rho_1(r_1, r_1) = \rho(r_1)
\]

The diagonal elements of the two-particle spin-less density matrix \( \rho_2(r_1, r_2, r_1, r_2) = \rho_2(r_1, r_2) \) are conventionally expressed by means of the pair-correlation function \( h(r_1, r_2) \):

\[
\rho_2(r_1, r_2) = \frac{1}{2} \rho(r_1)\rho(r_2) (1 + h(r_1, r_2))
\]
Exercise:

Show that:

\[ V_{ee} \equiv \int \psi^* (r_1, \cdots, r_N) \left| \sum_{i} \sum_{i<j} \frac{1}{|r_i - r_j|} \right| \psi (r_1, \cdots, r_N) \, dr_1, \cdots, dr_N = \int \int \frac{1}{r_{12}} \rho_2 (r_1, r_2) \, dr_1 \, dr_2 \]
Exchange-correlation hole: definition

Exchange correlation hole is defined as:

\[ \rho_{xc}(r_1, r_2) = \rho(r_2)h(r_1, r_2) \]

where, \( h(r_1, r_2) \) is the pair-correlation function:

\[ \rho_2(r_1, r_2) = \frac{1}{2} \rho(r_1)\rho(r_2) (1 + h(r_1, r_2)) \]

Since:

\[ \rho_{xc}(r_1, r_2) = \left( \frac{2\rho_2(r_1, r_2)}{\rho(r_1)} - \rho(r_2) \right) \]

\( \rho_{xc}(r_1, r_2) \) is called also exchange-correlation charge.

Using \( \rho_{xc}(r_1, r_2) \) we obtain:

\[ V_{ee} \equiv \langle \Psi | \hat{v}_{ee} | \Psi \rangle = \int \int \frac{1}{\rho_{12}} \rho_2(r_1, r_2) dr_1 dr_2 = J[\rho] + \frac{1}{2} \int \int \frac{1}{\rho_{12}} \rho(r_1)\rho_{xc}(r_1, r_2) dr_1 dr_2 \]

Note that \( V_{ee} - J[\rho] \) is one of the components of the exchange-correlation energy in the Kohn-Sham formulation of DFT (the difference is just \( T[\rho] - T_s[\rho] \)).
Properties of $\rho_{xc}(r, r')$

The exact exchange-correlation hole ($\rho_{xc}$) satisfies the sum rule:

$$\int \rho_{xc}(r_1, r_2) dr_2 = -1$$

**Exercise**

Derive the above relation.

1) Show that:

$$\rho_1(r'_1, r_1) = 2 \frac{N}{N-1} \int \rho_2(r'_1, r_2, r_1, r_2) dr_2$$

2) Use the definition of $\rho_{xc}(r_1, r_2)$
Properties of $\rho_{xc}(r, r')$ cnt.

The separate components of $\rho_{xc}(r, r')$:

$$\rho_{xc}(r, r') = \rho_x(r, r') + \rho_c(r, r')$$

are called: $\rho_x(r, r')$) is the Fermi hole and $\rho_c(r, r')$ is the Coulomb hole.

In the constrained search definition the partitioning of the total hole is unique. The functions $\Psi[\rho]$ and $\Psi_s[\rho]$ are available and can be used to evaluate $\rho_{xc}(r, r')$ ($\Psi[\rho]$) and $\rho_x(r, r')$ ($\Psi_s[\rho]$).

The exact holes satisfy the following conditions:

- $\rho_x(r, r') \leq 0$
- $\int \rho_x(r, r') dr' = -1$
- $\int \rho_c(r, r') dr' = 0$
Examples of $\rho_{xc}(\mathbf{r}, \mathbf{r}')$
Artificial system with modified Coulomb interactions (1)

The coupling parameter $\lambda$ determines the strength of the electron-electron repulsion. For $\lambda = 1$ the entire electron-electron repulsion is switched on, but all other values $0 \leq \lambda < 1$ correspond to an artificial reference system. Kohn-Sham system is a particular case $\lambda = 0$).

The functional $F[\rho]$, defined using the constrained search for the Kohn-Sham theory can be generalized for $0 < F[\lambda][\rho] \leq 1$ in a straightforward manner:

$$F[\lambda][\rho] = \min_{\psi \to \rho} \langle \psi | \hat{T} + \lambda \hat{V}_{ee} | \psi \rangle = \langle \psi^{\lambda}_{\rho} | \hat{T} + \lambda \hat{V}_{ee} | \psi^{\lambda}_{\rho} \rangle$$

where $\psi^{\lambda}_{\rho}$ is the N-electron wave function that minimizes $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$ and yields the density $\rho$.

**Properties of $F[\lambda][\rho]$**

$$F[\lambda=0][\rho] = T_s[\rho]$$

$$F[\lambda=1][\rho] = T[\rho] + V_{ee}[\rho]$$
Artificial system with modified Coulomb interactions (2)

From $\Psi_\rho^\lambda$, we get the following $\lambda$ dependent quantities:

- The diagonal elements of two-particle spinless density matrix:
  \[
  \rho^\lambda_2(r_1, r_2) = \frac{N(N - 1)}{2} \int \cdots \int \Psi_\rho^\lambda(r_1, ds_1, r_2, ds_2, \cdots, x_N) \Psi_\rho^\lambda(r_1, ds_1, r_2, ds_2, \cdots, x_N) ds_1, ds_2, dx_3 \cdots dx_N
  \]

- Pair-correlation function:
  \[
  \rho_2^\lambda(r_1, r_2) = \frac{1}{2} \rho(r_1) \rho(r_2) \left(1 + h^\lambda(r_1, r_2)\right)
  \]

- Exchange-correlation hole:
  \[
  \rho_{xc}^\lambda(r_1, r_2) = \rho(r_2) h^\lambda(r_1, r_2)
  \]

- Expectation value of the electron-electron repulsion:
  \[
  \langle \Psi_\rho^\lambda | \hat{v}_{ee} | \Psi_\rho^\lambda \rangle = \int \int \frac{1}{r_{12}} \rho^\lambda_2(r_1, r_2) dr_1 dr_2 = J[\rho] + \frac{1}{2} \int \int \frac{1}{r_{12}} \rho(r_1) \rho_{xc}^\lambda(r_1, r_2) dr_1 dr_2
  \]

Note that the functional $T_s[\rho]$ does not depend on $\lambda$. 
Averaged exchange-correlation hole: $\bar{\rho}_{xc}(r_1, r_2)$

Definitions of $\bar{\rho}_2(r_1, r_2)$ and $\bar{\rho}_{xc}(r_1, r_2)$:

\[
\bar{\rho}_2(r_1, r_2) = \int_{0}^{1} \rho_{2}^{\lambda}(r_1, r_2) d\lambda \\
\bar{\rho}_{xc}(r_1, r_2) = \rho(r_2) - \frac{\bar{\rho}_2(r_1, r_2)}{\rho(r_1)}
\]

From the definition of $E_{xc}[\rho]^1$

\[
E_{xc}[\rho] = V_{ee}[\rho] - J[\rho] + T[\rho] - T_s[\rho] = F_1[\rho] - F_0[\rho] - J[\rho] = \int_{0}^{1} d\lambda \frac{\partial F_{\lambda}[\rho]}{\partial \lambda} - J[\rho]
\]

The Hellman-Feynman theorem $\frac{\partial F_{\lambda}[\rho]}{\partial \lambda} = \langle \psi_{\lambda} \mid \hat{V}_{ee} \mid \psi_{\lambda} \rangle$ and the relation $\langle \psi_{\rho}^{\lambda} \mid \hat{v}_{ee} \mid \psi_{\rho}^{\lambda} \rangle = J[\rho] + \frac{1}{2} \int \int \frac{1}{r_{12}} \rho(r_1) \rho_{xc}^{\lambda}(r_1, r_2) dr_1 dr_2$ yield:

\[
E_{xc}[\rho] = \int_{0}^{1} d\lambda \langle \psi_{\rho}^{\lambda} \mid \hat{V}_{ee} \mid \psi_{\rho}^{\lambda} \rangle - J[\rho] = \int \int \frac{1}{r_{12}} \rho(r_1) \bar{\rho}_{xc}(r_1, r_2) dr_1 dr_2
\]

\(^1\)A silent assumption: $\rho$ is $v$-representable
Adiabatic-connection formula for $E_{xc}[\rho]$}

\[ E_{xc}[\rho] = \int \int \frac{1}{r_{12}} \rho(r_1)\bar{\rho}_{xc}(r_1, r_2) \, dr_1 \, dr_2 \]  

Eq. 1 opens new possibilities to develop better approximations for $E_{xc}[\rho]$ and also provides also the theoretical justification for hybrid schemes, in which the Kohn-Sham orbitals are used to evaluate (part of) the exchange energy.

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In the scheme proposed by Becke ⁴ ('half-and-half' approach), the integral
\[ \int_{0}^{1} (\rho_{xc}^{\lambda}(r_1, r_2)) d\lambda \]
is approximated by the average of two terms:

\[ \int_{0}^{1} (\rho_{xc}^{\lambda}(r_1, r_2)) d\lambda \approx \frac{1}{2} (\rho_{xc}^{0}(r_1, r_2) + \rho_{xc}^{1}(r_1, r_2)) \]

The numerical value of the term corresponding to \( \lambda = 0 \) can be evaluated exactly using the known Kohn-Sham orbitals - it is equal to the exchange energy calculated using Kohn-Sham orbitals.

The other term, corresponding to \( \lambda = 1 \) is not known. It is known to good accuracy (LDA or GGA for instance). Becke showed that for many properties of organic molecules the introduction of the explicit dependence of the exchange-correlation energy on the Kohn-Sham orbitals improves the obtained results.

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Currently, the hybrid functional known as B3 (Becke’s three parameter exchange functional) \(^5\) is one of the most commonly used functional (especially in organic chemistry). This functional is frequently combined with either LYP, or PW91 correlation functional. In the original publication the PW91 density functional was used for correlation. Most of current applications use LYP for this purpose. The B3LYP functional reads:

\[
E_{xc}^{B3LYP}(\{\phi_i\}) = (1 - a)E_{x}^{LSDA}[\rho] + aE_{x}^{'exact'}(\{\phi_i\}) + b(E_{x}^{B88}[\rho] - E_{x}^{LSDA}[\rho])
\]

\[
+ E_{c}^{VWN}[\rho] + c(E_{c}^{LYP} - E_{c}^{VWN}[\rho])
\]

where \(a, b, c\) are parameters fitted to thermochemical data in a learning set of molecules (\(a \approx 0.2, b \approx 0.7, c \approx 0.8\)).